NITROGEN RETENTION IN THE RIPARIAN ZONE OF WATERSHEDS

UNDERLAIN BY DISCONTINUOUS PERMAFROST

By

Jonathan A. O'Donnell

RECOMMENDED:

Chair, Advisory Committee

Chair, Biology and Wildlife Department

APPROVED:

Dean, College of Natural Science and Mathematics

Dean of the Graduate School

April 4, 2005

Date

NITROGEN RETENTION IN THE RIPARIAN ZONE OF WATERSHEDS UNDERLAIN BY DISCONTINUOUS PERMAFROST

A

THESIS

Presented to the Faculty

of the University of Alaska Fairbanks

in Partial Fulfillment of the Requirements

for the Degree of

MASTER OF SCIENCE

By

Jonathan A. O'Donnell, B.S.

Fairbanks, Alaska

May 2005

Abstract

Riparian zones function as important ecotones for reducing nitrate concentration in groundwater and inputs into streams. In the boreal forest of interior Alaska, permafrost confines subsurface flow through the riparian zone to shallow organic horizons, where plant uptake of nitrate and denitrification are typically high. Two research questions were addressed in this study: 1) how does riparian zone nitrogen retention vary in watersheds underlain by discontinuous permafrost, and 2) what is the contribution of denitrification to riparian zone nitrogen retention? To estimate the contribution of the riparian zone to watershed nitrogen retention, I analyzed groundwater chemistry using an end-member mixing model. To assess the importance of denitrification as a mechanism of nitrogen retention, I conducted field denitrification assays using the acetylene block technique. Over the summer, nitrogen retention averaged 0.75 and 0.22 mmol N m^{-2} d^{-1} in low and high permafrost watersheds, respectively. Compared with the fluvial export of nitrogen, the retention rate of nitrogen in the riparian zone is 10 – 15% of the loss rate in stream flow. Denitrification accounted for a small proportion (3%) of total nitrogen retention in the riparian zone. Variation in nitrogen retention between watersheds did not account for differences in stream nitrate concentration between watersheds.

Table of Contents

List of Figures

List of Tables

Preface

The thesis is in manuscript format, and has been divided into two chapters. Chapter 1 is a general review of the relevant topics related to riparian zone nitrogen retention. Topics include the factors regulating denitrification, the role of riparian zones as nutrient buffers, hydrologic models of riparian zone functioning, and permafrost hydrology. Chapter 2 has been formatted for submission to *Freshwater Biology*, an international peer-reviewed journal. This chapter contains specific methods, results, and conclusions drawn from this study.

I'd like to thank Emma Betts, Jessica Eichmiller, Nick Lisuzzo, and Jenny Rohrs for their help in the field and laboratory. I'd also like to thank Larry Hinzman and Knut Kielland, who served on my committee and who provided valuable comments on the manuscript. I'd particularly like to thank my advisor, Jay Jones, for his guidance throughout this study and the writing of this manuscript. Finally, I'd like to thank Chrissy Apodaca for her support and encouragement over the last year.

This research was part of the Bonanza Creek LTER (Long-Term Ecological Research) program (funded jointly by NSF grant DEB-0423442 and USDA Forest Service, Pacific Northwest Research Station grant PNW01-JV11261952-231).

Chapter 1. Introduction

Factors controlling denitrification

Denitrification is a microbially-mediated process whereby nitrate is reduced to gaseous nitrogen (NO, N_2O, N_2) under anoxic conditions. Environmental controls on denitrification have been identified in a number of studies (Tiedje 1988, Schipper et al. 1993). The primary factors that regulate denitrification rate are oxygen, nitrate, and organic carbon. There is also a suite of factors that indirectly influence denitrification, including soil particle size, soil moisture, temperature, and pH. Spatial and temporal variation of these parameters often accounts for the high variability of denitrification in soil (Clement et al. 2002).

The occurrence of denitrification in nature is largely restricted to anoxic and hypoxic habitats. Oxygen concentration in soil water is a function of both the supply of oxygen to soil habitats and the rate of oxygen consumption (Tiedje 1988). The movement of oxygen through the soil matrix is slowed by physical barriers (rocks, clay, sand), biological barriers (plant roots, organic debris), and water (Naiman and Décamps 1997). While the presence of water in soil pore spaces decreases the diffusion rate of oxygen, the movement of water through soil pores also serves as a vector of oxygen transport. The rate of oxygen consumption in soil is regulated by the heterotrophic respiration of organic carbon, which depletes soil of oxygen. Once oxygen becomes depleted, facultative bacteria begin to use nitrate as an alternative electron acceptor during the oxidation of organic matter (i.e., denitrification; Schlesinger 1997). In well-

drained soils where the diffusion of oxygen is fast, high rates of denitrification can persist in soil microsites, where heterotrophic respiration depletes oxygen locally in small pore spaces (Parkin 1987).

Nitrate supply is also an important control on the rate of denitrification (Tiedje 1988, Schipper et al. 1993, Holmes et al. 1996). The most common source of nitrate is from nitrogen mineralization and the subsequent oxidation via nitrification. Groundwater flow paths often serve as hydrologic conduits, delivering nitrate to the site of denitrification. Nitrate availability in soil and groundwater is regulated by a number of different processes. Plant uptake and microbial assimilation of nitrate compete with denitrifiers for the available pool nitrate in soil and groundwater. Dissimilatory nitrate reduction to ammonia is an alternative microbial pathway that results in the production of ammonium instead of dinitrogen gas (Tiedje 1988). Nitrate is also a highly mobile ion, and thus is susceptible to leaching losses.

Carbon limitation of denitrification has been observed in a number of studies (Starr and Gillham 1993, Hedin et al. 1998, Hill et al. 2000). Organic carbon serves as an electron donor for denitrification. The primary sources of dissolved organic carbon (DOC) to denitrifiers are the decomposition and leaching of particulate organic matter, and the production of organic matter via plant roots. As plants allocate resources to the production of root biomass, a portion of the organic carbon is lost to the soil. This process, which is known as rhizodeposition (Whipps and Lynch 1985), can fuel microbial processes in the rhizosphere, such as denitrification (Brar 1972, Schade et al. 2001).

A number of other factors indirectly influences the occurrence and rate of

denitrification in nature. Soil moisture content can determine the extent of anoxic zones in soil that allow for the reduction of nitrate via denitrification (Groffman et al. 1996, Clement et al. 2002). Soil texture is also correlated with denitrification rate; Pinay et al. (2000) measured a high rate of denitrification in fine textured soils (high silt + clay content). In soil with < 65% silt and clay content, no measurable denitrification was detected. Temperature is also an important control regulating the rate of denitrification (Groffman et al. 1996, Holmes et al. 1996). Whereas dinitrogen gas is the primary product of denitrification, a small portion of nitrous oxide (N_2O) is also produced. The relative proportion of N_2O produced relative to N_2 is a function of pH (Firestone et al. 1980, Stark et al. 2002).

In this study, denitrification rates were measured using the acetylene block technique (Yoshinari and Knowles 1976). Acetylene (C_2H_2) is structurally similar to N_2O, and can block the reduction of N_2O to dinitrogen gas (N_2) by inhibiting the activity of nitrous oxide reductase. In denitrification incubations using the acetylene block technique, the accumulation of N_2O represents the total production of N_2 and N_2O from denitrification. An advantage of the acetylene block technique is that N_2O can measured at low concentrations on a gas chromatograph because the ambient background concentration of N_2O is low, unlike that of N_2. One potential problem associated with the acetylene block technique is that acetylene also inhibits nitrification. Acetylene blocks nitrification by reacting with the active site of ammonium monooxygenase, the ammonia-oxidizing enzyme of nitrifiers (Hyman and Wood 1985). Upon the removal of acetylene, the enzyme remains inactive. Thus, only synthesis of new enzymes will restore

nitrification activity. By blocking nitrification, acetylene cuts off the production of nitrate for denitrifying bacteria. In systems where denitrification is nitrogen-limited, the acetylene block technique can underestimate unamended denitrification rate (Tiedje 1988).

Riparian zones as nutrient filters

Riparian zones are important locations for reducing nitrate in groundwater and the input into streams (Lowrance et al. 1984, Peterjohn and Correll 1984). Plant uptake, microbial immobilization, and denitrification are the primary mechanisms accounting for the removal of nitrate from groundwater. Plant uptake temporarily retains nitrogen via storage in biomass. Foliar nitrogen is returned to the available soil nitrogen pool when the plant dies and is mineralized. Similarly, microbial assimilation of nitrogen temporarily retains nitrogen in bacterial biomass until cell death and decomposition release nitrogen back into the soil. In contrast to plant uptake and microbial assimilation, denitrification results in the permanent loss of nitrogen from ecosystems to the atmosphere as N_2.

There are several important features of riparian soil that influence the capacity to function as nutrient filters. Riparian zones are located prominently within the landscape, linking terrestrial and aquatic ecosystems. Thus, despite occupying a small area of land relative to the entire catchment, riparian processing of nutrients is particularly important (Gregory et al. 1991). Riparian soil is typically rich in organic carbon, which can serve as an electron donor for heterotrophic processes such as denitrification (Schipper et al.

1993). Riparian soil is often water-saturated relative to upland soil, which leads to the anoxic soil condition conducive for denitrification. Whereas nitrification and denitrification are usually coupled in upland soil, saturated riparian soil typically requires an external source of nitrate from groundwater or upland soil to sustain denitrification (Schipper et al. 1993). Riparian soils often function as denitrification "hotspots" (McClain et al. 2003), in part due to the convergence of nitrate-rich groundwater flow paths with anoxic soils rich in organic carbon (Hedin et al. 1998, Hill et al. 2000).

The functional role of the riparian zone as a nutrient filter varies across seasons. Seasonal fluctuations in water table height determine the extent of anoxic zones in soil, which in turn, regulates the occurrence of denitrification (Hefting et al. 2004). The nitrogen uptake by plants is also influenced by seasonal shifts in water availability (Naiman and Décamps 1997). Riparian zones are typically less effective at buffering against fluvial nitrogen loss during winter and seasonal transitions (Bechtold et al. 2003, Sickman et al. 2003). Extreme cold in winter can lead to long periods of plant dormancy, fine root mortality (Ruess et al. 1998), enhanced nitrification and nitrate loss (Groffman et al. 2001), and decreased denitrification due to freeze damage suffered by denitrifiers (Cooke 1990). Spring nitrate pulses observed in stream water are typically attributed to increased nitrate leaching during snowmelt (Groffman et al. 1993, Bechtold et al. 2003).

Models of riparian zone function

Several recent studies have examined the linkages between biogeochemical processes and hydrologic conditions in the riparian zone (Hedin et al. 2000, Devito et al.

2000, Vidon and Hill 2004). Hill (2000) presented a conceptual model of riparian zone functioning in relation to watershed hydrogeology and stream chemistry (Fig. 1). This perspective has focused considerable attention on the hydrologic links between the riparian zone and watershed, and the internal hydrology of the riparian zone (Hill 2000).

Biogeochemical transformations within riparian zones are influenced by both watershed hydrology and hydraulics of stream channels (Triska et al. 1993). In many watersheds, subsurface flow is unidirectional from uplands, through the riparian zone to the stream channel. However, in some cases, subsurface flow in the riparian zone is bidirectional, characterized by the mixing of hyporheic water derived from the stream with groundwater flowing through the riparian zone (Hinzman et al. 2000). Riparian zones with thick aquifers can also receive hydrologic input from the upwelling of groundwater directly to the surface of riparian soil (Hill 2000). Hedin et al. (1998) observed high rates of denitrification in regions where oxidized near-stream water converged with groundwater from reduced inland environments, and rapid upwelling of deep groundwater intersected slow groundwater flow paths through shallow soil horizons.

In addition to hydrologic linkages with upland and stream habitats, nitrogen retention is also regulated by the internal hydrology of the riparian zone. Nitrate loss from riparian groundwater is typically high where an impermeable geologic feature confines subsurface flow to shallow organic soil (Cooper 1990, Hill 1996, Clement et al. 2002). Plant uptake is enhanced where shallow lateral flow promotes the interaction between groundwater nitrate and the rooting zone of plants. Denitrification is typically

high in shallow soil horizons, where large stores of labile organic carbon are available to microbial communities. However, high rates of denitrification have been observed in deeper, permeable riparian soils, where nitrate-rich groundwater flowpaths intersect groundwater high in DOC (Hill et al. 2000).

Permafrost and hydrology

Permafrost is defined as ground that has remained at or colder than 0°C for at least two consecutive years (Davis 2001). Permafrost underlies nearly 22% of the land area of North America (Davis 2001). In northern Alaska and Canada, land areas are underlain by continuous permafrost. In the boreal forest of interior Alaska, land is underlain largely by discontinuous permafrost (Fig. 2). The distribution of permafrost is a function of aspect: north-facing slopes are underlain by permafrost and south-facing slopes are typically permafrost-free.

Permafrost has a profound influence on watershed hydrology (Woo 1986). Permafrost is largely impermeable to groundwater flow, and thus prevents percolation of water into deeper soil horizons. In regions with permafrost, most hydrologic activity is confined to the active layer, or the soil above the permafrost table that seasonally thaws and freezes. At high latitudes, many hydrologic and biologic processes become dormant during the long winter season. Groundwater flow and storage in regions with permafrost are confined largely to the active layer, although a small portion of groundwater occurs in taliks within permafrost (intrapermafrost groundwater) and below the permafrost table (subpermafrost groundwater; Woo 2000). The storage capacity of groundwater in the

active layer increases during the summer as thaw depth increases. Following snowmelt, groundwater flows laterally through shallow organic soil horizons. As thaw depth increases over the summer, groundwater flows through deeper mineral soil horizons. However, flow through organic horizons following large rain storms can still occur.

In the boreal forest, the presence or absence of permafrost also has significant effect on stream hydrology. Streams draining permafrost-dominated watersheds have a "flashy" hydrology, characterized by high stormflows and low baseflow (Woo 1986). Streams draining permafrost-free watersheds are characterized by reduced stormflows and more sustained baseflows (Woo 1986). The difference in stream hydrology among watersheds with varying extents of permafrost can be attributed to several factors. First, the presence of permafrost confines the majority of flow to the organic soil horizon and moss layer, whereas permafrost-free areas allow infiltration of water to deeper mineral horizons. The flow rate of water through the organic layer is orders of magnitude higher than through mineral soil (Woo 2000). Second, in permafrost-dominated catchments, zones of preferential flow, such as macropores, inter-hummock zones, and water tracks, enhance the delivery of water through the catchment to the stream (Carey and Woo 2000). Where they exist, these features allow near-surface flow to bypass the soil matrix and consequently, increase hydrologic inputs to streams. Finally, increased storage of groundwater in permafrost-free uplands allows for longer residence time of water in the catchment.

Caribou Poker Creeks Research Watershed (CPCRW)

In interior Alaska, stream chemistry varies substantially among watersheds with varying extents of permafrost (MacLean et al. 1999, Jones et al. 2005). In CPCRW, a stream draining a high permafrost watershed (53% of watershed area underlain by permafrost) had enriched DOC concentrations and low dissolved mineral concentrations (MacLean et al. 1999). This pattern was attributed to the presence of permafrost, which confines groundwater flow to shallow organic soil and thus, runoff chemistry was not modified by the mineral soil horizon (MacLean et al. 1999). In contrast, a stream draining a low permafrost watershed (3% of watershed area underlain by permafrost) had lower DOC concentrations and higher dissolved mineral concentrations. The absence of permafrost in this watershed allowed for deeper groundwater flow paths through mineral horizons, where absorption presumably reduced DOC concentrations (McDowell and Wood 1984).

Stream nitrate concentration also varies between watersheds with varying extents of permafrost. In CPCRW, stream nitrate concentration was over two-fold greater in the low permafrost watershed than the high permafrost watershed (MacLean et al. 1999, Jones et al. 2005). This variation in stream nitrate concentration suggests that watershed or in-stream controls on nitrate also may vary between watersheds. MacLean et al. (1999) hypothesized that denitrification in the riparian zone is an important mechanism regulating stream nitrogen concentration in CPCRW. In addition, they hypothesized that the slow movement of water through the mineral horizon in the low permafrost watershed

allows for the greater potential for denitrification. Slow flow rates presumably allow for the depletion of oxygen in groundwater, thus creating ideal conditions for denitrification.

The mechanisms accounting for the variation in stream nitrogen concentration have not been adequately characterized in this system. In the present study, nitrogen retention in the riparian zone was compared between a high permafrost watershed and a low permafrost watershed in interior Alaska. The study design was confined to the valley bottom of each watershed, both of which are underlain by permafrost. However, upland areas differ between these watersheds with respect to permafrost extent and thickness, depth of groundwater flow paths, stand type, soil temperature, soil nitrogen, and soil carbon pools. These features likely influence nitrogen transformations in the riparian zone of these two watersheds.

Processes occurring in uplands likely have important implications for processes occurring within the riparian zone. In interior Alaska, stand type in upland forests varies substantially among watersheds with varying extents of permafrost. In CPCRW, deciduous forests (*Betula papyrifera* and *Populus termuloides*) dominate south-facing, permafrost-free slopes. In permafrost-dominated north-facing slopes, coniferous forests of white spruce (*Picea glauca*) and black spruce (*P. mariana*) dominate. Soil temperature is typically lower on north-facing slopes. The distribution of permafrost and vegetation across boreal forest landscapes has important implications for the down-slope transport of nitrate and carbon. For instance, colder soils in black spruce stands result in

reduced decomposition of organic matter, reduced plant activity, and low rates of nitrogen cycling (Van Cleve et al. 1983).

Patterns of nitrate delivery from upland forests to the riparian zones in CPCRW appear to vary between watersheds. MacLean et al. (1999) observed higher soil inorganic nitrogen concentrations in deciduous uplands of the low permafrost watershed than in the coniferous uplands of the high permafrost watershed. The difference in soil inorganic nitrogen between stand types is largely due to differences in nutrient inputs in litterfall, soil temperature and rates of decomposition (Van Cleve et al. 1983). Variation in nitrate input from upland forests to the riparian zone is likely an important factor influencing rates of nitrogen retention in the riparian zone.

The quantity and quality of DOC transported from upland forests to the riparian zone also appear to vary between watersheds in CPCRW. In CPCRW, black spruce communities, which dominate in high permafrost watersheds, produce highly recalcitrant organic matter relative to the hardwood stands that dominate in the low permafrost watershed uplands (Van Cleve et al. 1983). The proportion of labile DOC is relatively low in boreal forest streams (ranging from 2–9%, Jones unpublished data, Kawahigashi et al. 2004), suggesting that DOC quality may be more important than quantity in predicting nitrate loss. Baker et al. (2004) found a significant correlation between denitrification rate and the concentration of low molecular weight organic acids. The quality of DOC inputs to the riparian zone in this system may be a reflection of vegetation patterns in upland forest.

In this study, nitrogen retention in the riparian zone was compared in two watersheds with differing extents of permafrost to determine if nitrogen transformations in the riparian zone account for the observed variation in stream nitrogen concentration. Nitrogen retention in this study refers to the removal of nitrate from groundwater and input to streams. In this context, the primary mechanisms of riparian nitrogen retention are plant uptake and denitrification. The relative importance of each mechanism is unclear in most watersheds. A network of groundwater wells was installed in each watershed (Fig. 5). To estimate total riparian nitrogen retention, groundwater chemistry was analyzed using an end-member mixing model. To estimate the contribution of denitrification to riparian zone nitrogen retention, denitrification rate was measured using the acetylene block technique on intact soil cores. Together, these approaches help to assess the importance of the riparian zone in regulating nitrogen concentration in streams.

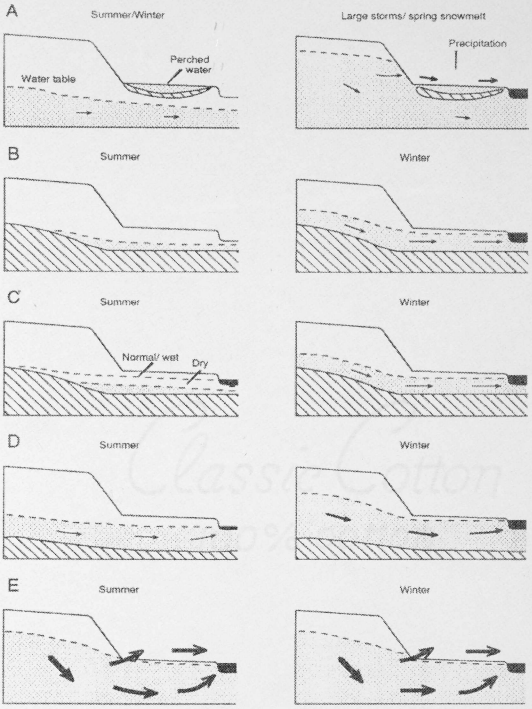

Figure 1. Conceptual model illustrating varying ground water flow systems in riparian zones of headwater catchments (from Hill 2000). (A) Perched aquifer riparian zone. (B) Thin aquifer riparian zone. (C) Thin aquifer-rain dependent riparian zone. (D) Intermediate aquifer riparian zone. (E) Thick aquifer riparian zone. The different sized arrows represent small, medium, and large groundwater fluxes. The gray area represents groundwater, and the area with diagonal lines represents an impermeable layer.

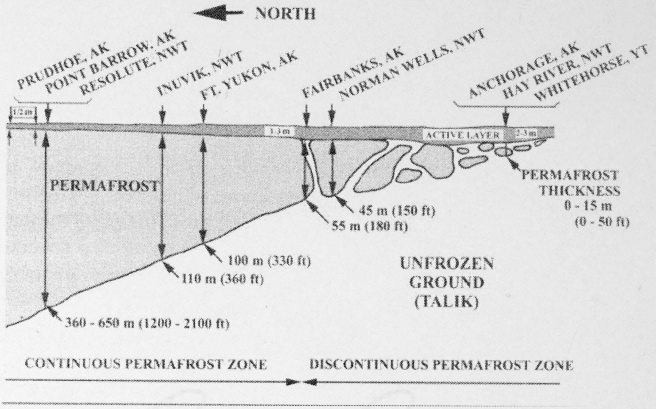

Figure 2. Transect running north and south through Alaska, USA. The diagram illustrates the gradient of permafrost, ranging from continuous to discontinuous permafrost (from Davis 2001).

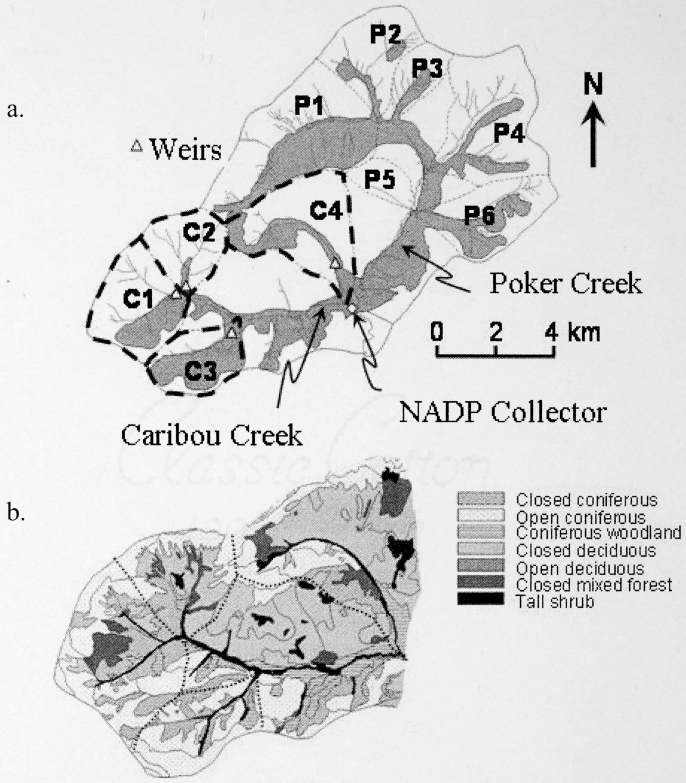

Figure 3. Caribou Poker Creeks Research Watershed map of permafrost (panel a) and vegetation distribution (panel b) (from www.lter.uaf.edu; Bonanza Creek Long Term Ecological Research Program).

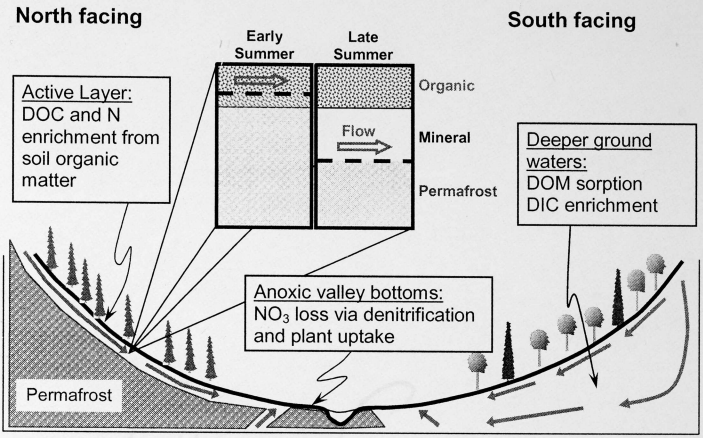

Figure 4. Conceptual model of permafrost, hydrology, and biogeochemistry (adopted from MacLean et al. 1999). The interaction between permafrost and stand type in upland forests influences patterns of nitrate and carbon delivery to the riparian zone. Soil inorganic nitrogen pools are higher in the warmer south-facing deciduous uplands than the cooler, wetter, north-facing coniferous uplands. Permafrost in upland forests promotes lateral transfer of DOC to the riparian zone and stream. DOC transfer is reduced from permafrost-free uplands to the riparian zone due to DOC sorption in mineral soils. The presence of permafrost in the valley bottom of watersheds promotes nitrate removal from groundwater by confining groundwater flow to shallow organic horizons, where plant uptake and denitrification are high.

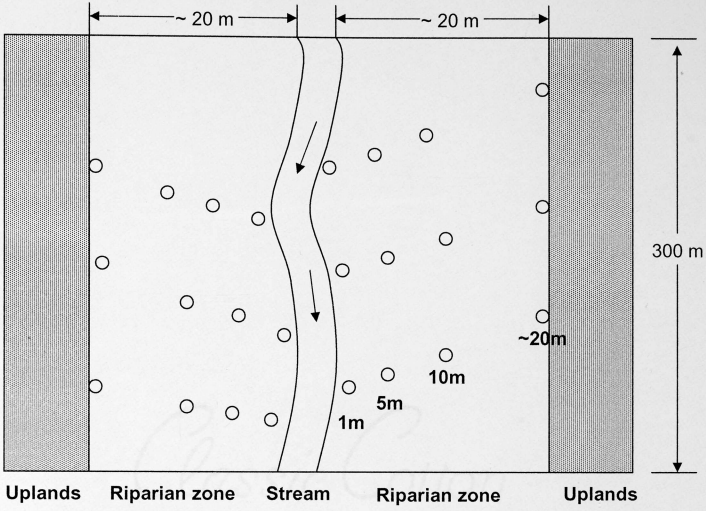

Figure 5. Schematic diagram of well transects in Caribou Poker Creeks Research Watershed (CPCRW). Six transects consisting of four wells were installed in both a high and low permafrost watershed along a 300 m reach of stream. Wells (symbolized by circles) were installed to a depth of 1 m. The first three wells were installed at 1, 5 and 10 m from the stream channel. The last well was installed at the upland-riparian boundary, which typically was between 15 and 30 m from the stream, depending on the width of the valley bottom. The arrows in the stream channel indicate the direction of flow.

References

Bechtold, J.S., R.T. Edwards, and R.J. Naiman. 2003. Biotic versus hydrologic control over seasonal nitrate leaching in a floodplain forest. Biogeochemistry 63: 53-72.

Brar, S.S. 1972. Influence of roots on denitrification. Plant and Soil 37: 267-270.

Carey, S.K., and M.-K. Woo. 2000. The role of soil pipes as a runoff mechanism, Subarctic Yukon, Canada. Journal of Hydrology 233: 206-222.

Clemént, J.-C., G. Pinay, and P. Marmonier. 2002. Seasonal dynamics of denitrification along topohydrosequences in three different riparian wetlands. Journal of Environmental Quality 31: 1025-1037.

Cooke, J.G. 1990. Rapid freezing effects on nitrification and denitrification enzyme activity in saturated soil and aquatic sediments. Soil Biology and Biochemistry 22: 1171-1172.

Cooper, A. B. 1990. Nitrate depletion in a riparian zone and stream channel of a small headwater catchment. Hydrobiologia 202: 13-26.

Davis, N. 2001. Permafrost: a Guide to Frozen Ground in Transition. University of Alaska Press, Fairbanks, Alaska, USA.

Devito, K.J., D. Fitzgerald, A.R. Hill, and R. Aravena. 2000. Nitrate dynamics in relation to lithology and hydrologic flowpath in a river riparian zone. Journal of Environmental Quality 29: 1-14.

Firestone, M.K., R.B. Firestone, and J.M. Tiedje. 1980. Nitrous oxide from soil denitrification: factors controlling its biological production. Science 208: 749-751.

Gregory, S.V., F.J. Swanson, W.A. McKee, and K.W. Cummins. 1991. An ecosystem perspective of riparian zones. Bioscience 41: 540-551.

Groffman, P.M., G.C. Hanson, A.J. Gold, and W.M. Nelson. 1996. Microbial nitrate processing in shallow groundwater in a riparian forest. Journal of Environmental Quality 25: 1309-1316.

Groffman, P.M., C.T. Driscoll, T.J. Fahey, J.P. Hardy, R.D. Fitzhugh, and G.L. Tierney. 2001. Colder soils in a warmer world: a snow manipulation study in a northern hardwood forest ecosystem. Biogeochemistry 56: 135-150.

Hedin, L.O., J.C. von Fischer, N.E. Ostrom, B.P. Kennedy, M.G. Brown, and G.P. Robertson. 1998. Thermodynamic constraints on nitrogen transformations and other biogeochemical processes at soil-stream interfaces. Ecology 79: 684-703.

Hefting, M., J.C. Clément, D. Dowrick, A.C. Cosandey, S. Bernal, C. Cimpian, A. Tatur, T.P. Burt, and G. Pinay. Water table elevation controls on soil nitrogen cycling in riparian wetlands along a European climatic gradient. Biogeochemistry 67: 113-134.

Hill, A.R. 2000. Stream Chemistry and Riparian Zones. Pages 83-110 *in* J.B. Jones and P.J. Mulholland, editors. Streams and Ground Waters. Academic, San Diego, California, USA.

Hill, A. R., K. J. Devito, S. Campagnolo, and K. Sanmugadas. 2000. Subsurface denitrification in a forest riparian zone: interactions between hydrology and supplies of nitrate and organic carbon. Biogeochemistry 51: 193-223.

Hinzman, L.D., M. Wegner, and M.R. Lilly. 2000. Hydrologic investigations of ground-water and surface-water: interactions in subarctic Alaska. Nordic Hydrology 5: 339-356

Holmes, R.M., J.B. Jones, S.G. Fisher, and N.B. Grimm. 1996. Denitrification in a nitrogen-limited stream ecosystem. Biogeochemistry 33: 125-146.

Hyman, M.R., and P.M. Wood. 1985. Suicidal inactivation and labeling of ammonia mono-oxygenase by acetylene. The Biochemical Journal 227: 719-725.

Jones, J.B., K.C. Petrone, J.C. Finlay, L.D. Hinzman, and W.R. Bolton. 2005. Nitrogen loss from watershed of interior Alaska underlain with discontinuous permafrost. Geophysical Research Letters 32:L02401, 10.1029/2004GL021734.

Kawahigashi, M., K. Kaiser, K. Kalbitz, A. Rodionov, and G. Guggenberger. 2004. Dissolved organic matter in small streams along a gradient from discontinuous to continuous permafrost. Global Change Biology 10: 1576-1586.

Lowrance, R. R., R. L. Todd, and L.E. Asmussen. 1984. Riparian forests as nutrient filters in agricultural watersheds. Bioscience 34: 374-377.

MacLean, R., M. W. Oswood, J.G. Irons, and W.H. McDowell. 1999. The effect of permafrost on stream biogeochemistry: a case study of two streams in the Alaskan (USA) taiga. Biogeochemistry 47: 239-267.

McClain, M.E., E.W. Boyer, C.L. Dent, S.E. Gergel, N.B. Grimm, P.M. Groffman, S.C. Hartman, J.W. Harvey, C.A. Johnston, E. Mayorga, W.H. McDowell, and G. Pinay. Biogeochemical hot spots and hot moments at the interface of terrestrial and aquatic ecosystems. Ecosystems 6: 301-312.

Naiman, R.J., and H. Décamps. 1997. The ecology of interfaces: riparian zones. Annual Review of Ecology and Systematics 28: 621-658.

Parkin, T.B. 1987. Soil microsites as a source of denitrification variability. Soil Science Society of America Journal 51: 1194-1199.

Peterjohn, W. T., and D. L. Correll. 1984. Nutrient dynamics in an agricultural watershed: observations on the role of a riparian forest. Ecology 65: 1466-1475.

Pinay, G., V.J. Black, A.M. Planty-Tabacchi, B. Gumiero, and H. Décamps. 2000. Geomorphic control of denitrification in a large river floodplain soils. Biogeochemistry 30: 9-29.

Post, W.M., W.R. Emanuel, P.J. Zinke, and A.G. Stangenberger. 1982. Soil carbon pools and world life zones. Nature 298: 156-159.

Reuss, R.W., R.L. Hendrick, and J.P. Bryant. 1998. Regulation of fine root dynamics by mammalian browsers in early successional Alaskan taiga forests. Ecology 79: 2706-2720.

Schade, J.D., S.G. Fisher, N.B. Grimm, and J.A. Seddon. 2001. The influence of a riparian shrub on nitrogen cycling in a Sonoran Desert stream. Ecology 82: 3363-3376.

Schipper, L.A., A.B. Cooper, C.G. Harfoot and W.J. Dyck. 1993. Regulators of denitrification in an organic riparian soil. Soil Biology and Biochemistry 25: 925-933.

Schlesinger, W.H. 1997. Biogeochemistry: An Analysis of Global Change. San Diego: Academic Press.

Serreze, M.C., J.E. Walsh, F.S. Chapin, T. Osterkamp, M. Dyurgerov, V. Romanovsky, W.C. Oechel, J. Morison, T. Zhang, and R.G. Barry. 2000. Observational evidence of recent change in the northern high latitude environment. Climate Change 46: 159-207.

Stark, J.M., D.R. Smart, S.C. Hart, and K.A. Haubensak. 2002. Regulation of nitric oxide emissions from forest and rangeland soils of western North America. Ecology 83: 2278-2292.

Starr, R.C., and R.W. Gillham. 1993. Denitrification and organic carbon availability in two aquifers. Ground Water 31: 934-947.

Tiedje, J.M. 1988. Ecology of denitrification and dissimilatory nitrate reduction to ammonium. Pages 179-244 *in* A.J.B. Zehnder, editor. Biology of Anaerobic Microorganisms. John Wiley & Sons, New York, New York, USA.

Triska, F.J., J.H. Duff, and R.J. Avanzino. 1993. Patterns of hydrological exchange and nutrient transformation in the hyporheic zone of a gravel bottom stream. Freshwater Biology 29: 259-274.

Van Cleve, K., L. Oliver, R. Schlentner, L.A. Viereck, and C.T. Dyrness. 1983. Productivity and nutrient cycling in taiga forest ecosystems. Canadian Journal of Forest Research 13: 747-767.

Vidon, P., and A.R. Hill. 2004. Denitrification and patterns of electron donors and acceptors in eight riparian zones with contrasting hydrogeology. Biogeochemistry 71: 259-283.

Vitousek, P.M., J.D. Aber, R.W. Howarth, G.E. Likens, P.A. Matson, D.W. Schindler, W.H. Schlesinger, and D.G. Tilman. 1997. Technical report: human alteration of the global nitrogen cycle: sources and consequences. Ecological Applications 7: 737-750.

Whipps, J.M., and J.M. Lynch. 1985. Energy losses by the plant in rhizodeposition. Annual Proceedings of the Phytochemical Society of Europe 26: 59-71.

Woo, M.-K. 1986. Permafrost hydrology in North America. Atmosphere-Ocean 24: 201-234.

Woo, M.-K. 2000. Permafrost and hydrology. Pages 57-96 *in* M. Nuttall and T.V. Callghan, editors. The Arctic: Environment, People, Policy. Harwood Academic Publishing, Amsterdam, The Netherlands.

Yoshinari, T., and R. Knowles. 1976. Aceytlene inhibition of nitrous oxide reduction by denitrifying bacteria. Biochemical and Biophysical Research Communications 69: 705-710.

Chapter 2. Nitrogen Retention in the Riparian Zone of Watersheds Underlain by Discontinuous Permafrost[1]

Summary

1. Riparian zones function as important ecotones for reducing nitrate concentration in groundwater and inputs into streams. In the boreal forest of interior Alaska, permafrost confines subsurface flow through the riparian zone to shallow, highly organic soils, where plant uptake and denitrification is typically high.
2. In this study, nitrogen retention was examined in the riparian zone of a high permafrost watershed (53% of land area underlain by permafrost) and a low permafrost watershed (~ 3% permafrost). To estimate the contribution of the riparian zone to watershed nitrogen retention, we analyzed groundwater chemistry using an end-member mixing model. To assess the importance of denitrification as a mechanism of nitrogen retention, we conducted field denitrification assays using the acetylene block technique.
3. Stream nitrate concentration was over two-fold greater in the low permafrost watershed than the high permafrost watershed. Nitrate in riparian groundwater was not significantly different between watersheds, averaging 13 μM overall. Nitrogen retention averaged 0.75 and 0.22 mmol N m^{-2} d^{-1} in low and high permafrost watersheds, respectively, over the summer. Compared with fluvial export of nitrogen, the retention rate of nitrogen in the riparian zone was 10 – 15% of the loss rate in stream flow.

[1] Submitted as O'Donnell, J.A. and J.B. Jones. Nitrogen retention in the riparian zone of watersheds underlain by discontinous permafrost. *Freshwater Biology.*

4. Denitrification rate did not vary between watersheds, with an overall average of 113 nmol N m^{-2} d^{-1}. Denitrification accounted for a small proportion (3%) of total nitrogen retention in the riparian zone.
5. Nitrogen retention processes in the riparian zone did not vary between watersheds and did not appear to account for the observed differences in stream nitrate concentration between watersheds.

Introduction

Riparian zones can be important sites for reducing nitrogen concentration in groundwaters and the input into streams (Lowrance et al. 1984, Peterjohn and Correll 1984, Cooper 1990). Assimilation by plants and microbes, and consumption via denitrification, are the primary mechanisms accounting for the loss of nitrate as ground water flows through riparian zones. In the boreal forest of interior Alaska, terrestrial primary production is commonly nitrogen limited (Van Cleve et al. 1983, Schlesinger 1997), and thus plant assimilation in the riparian zone is likely an important sink. Further, nitrate loss via denitrification is generally enhanced in riparian zones where anoxic conditions and soil rich in organic matter provide optimal conditions (Hedin et al. 1998, Devito et al. 2000, Hill et al. 2000, Sobczak et al. 2002).

In the boreal forest of interior Alaska, watersheds are underlain by discontinuous permafrost, which is an important feature controlling watershed hydrology and the flow of water through the riparian zone (Slaughter and Kane 1979, Haugen et al 1982). Permafrost affects watershed hydrology by confining the majority of groundwater flow to shallow organic soil horizons (Woo 1986). Where permafrost is absent, soil water may infiltrate into deeper mineral soil horizons. Over the summer season, change in thaw depth within the active layer (soil above permafrost that seasonally thaws and freezes) allows groundwater flow to shift from organic to mineral horizons (Carey 2003). This shift in flow from organic to mineral horizons likely impacts rates and the major transformations of nitrogen in the riparian zone (Hill 1996).

The following research questions were addressed in two boreal forest catchments with varying extents of permafrost: 1) how does riparian zone nitrogen retention vary in watersheds with varying extents of permafrost, 2) what is the contribution of denitrification to riparian zone nitrogen retention? We hypothesized that permafrost influences groundwater nitrate loss by regulating the depth of groundwater flowpaths and, thus, the interaction with the organic soil horizon. To address these questions and this hypothesis, we used two approaches. First, groundwater chemistry was analyzed in two boreal forest catchments using an end member mixing model to calculate loss and production of solutes as water flowed through the riparian zone. This method provided an estimate of the contribution of the riparian zone to N retention within the watershed. Second, loss of nitrate in the riparian zone via denitrification was quantified through a series of denitrification field assays. Controls on denitrification were assessed by manipulating nitrogen and carbon availability in a laboratory assay.

Methods

Study site

The research was conducted in the Caribou Poker Creeks Research Watershed (CPCRW), which is located approximately 50 km northeast of Fairbanks, Alaska, and is associated with the Bonanza Creek Long Term Ecological Research Program (BNZ LTER). The watershed is characterized by rolling forested hills with saturated soils in valley bottoms. Vegetation patterns in the CPCRW vary with aspect and location across the landscape. North-facing slopes are dominated by black spruce (*Picea mariana)* and

white spruce (*P. glauca).* South facing-slopes are dominated by deciduous forests of paper birch (*Betula papyrifera)* and quaking aspen (*Populus tremuloides*). Vegetation in the valley bottom is distinct from upland forests. Valley bottom widths typically range from 50-75 m and are characterized by vegetation dominated by dwarf birch (*B. nana)*, bog blueberry (*Vaccinium uliginosum*), willow (*Salix* spp.), and to a lesser extent thin-leaf alder (*Alnus tenuifolia*).

In this study, two catchments with different permafrost extents were studied. The distribution of permafrost in Interior Alaska is largely a function of aspect and winter temperature, with north-facing slopes and valley bottoms generally underlain by permafrost (Viereck et al. 1983). Approximately 3% of the low permafrost watershed (previously reported as C2) was underlain by permafrost, whereas approximately 53% of the high permafrost watershed (C3) was underlain by permafrost (Rieger et al. 1972). Active layer depth reaches a maximum in August or September (Van Cleve et al 1981).

Stream discharge was measured over the study period using permanently installed flumes near the mouth of each watershed. Stream stage height was recorded with a datalogger (Campbell Scientific, Inc.) and then converted to discharge using rating equations (L.D. Hinzman and W.R. Bolton, University of Alaska Fairbanks, unpublished data).

Groundwater chemistry and hydrologic fluxes

We analyzed groundwater chemistry and hydrology by: (1) measuring groundwater chemistry using riparian zone wells, (2) identifying hydrologic sources

contributing to riparian zone ground water, and (3) using the results from an end-member mixing model in conjunction with nitrate and dissolved organic carbon (DOC) concentrations to calculate solute retention in the riparian zone. The end-member mixing model provided a prediction of nitrate and DOC concentrations in the absence of catchment biological processes.

Groundwater wells were installed in each watershed in April 2003 in transects (n = 6) that extended laterally from the stream-riparian interface to the riparian-upland boundary. Transects consisted of four wells each. The first three wells were installed at distances from the steam channel of 1, 5 and 10 m. The last well was installed at the edge of the valley bottom adjacent to the hill slope at distances from 15 to 30 m depending on the valley bottom width, as defined by the transition in vegetation type. Transects spanned a 300 m reach of stream in both watersheds. Wells were constructed of PVC pipe (1.25 cm ID) that were installed to a depth of 1 m; wells were perforated with 3 mm holes spaced every 5 cm from 10 to 95 cm below the soil surface. We collected stream and groundwater samples were collected every two weeks in 2003 from May 22 to August 11. Groundwater samples were stored at 4°C until analysis. Additionally, we measured thaw depth in conjunction with collection of groundwater samples at each well location by inserting a graduated stainless-steel depth probe into the soil until permafrost was contacted (thaw depth was also measured in 2004).

Groundwater nitrate production/loss

End member mixing model – The spatial variation in conservative solutes such as calcium in well water indicated that that direction of groundwater flow was not simply from upslope towards the stream through the riparian zone. Accordingly, mixing of stream and groundwater in the riparian zone was characterized using calcium in a two end-member mixing model (Genereux et al 1993) with an additional term for concentration effects due to evapotranspiration and partitioning of solutes between frozen and unfrozen phases of groundwater (i.e., exclusion; Zukowski and Tumeo 1991). Thus for the end-member mixing model, the following equations were simultaneously solved

$$1 = f_{sw} + f_{gw} \quad (1)$$

$$Ca_{(\%)well} = f_{sw} Ca_{(\%)sw} + f_{gw} Ca_{(\%)gw} \quad (2)$$

$$[Ca]_{well} = (f_{sw} [Ca]_{sw} + f_{gw} [Ca]_{gw})E \quad (3)$$

where f is the fraction of well water derived from stream (sw) and ground water (gw), $Ca_{(\%)}$ is the proportion of calcium relative to the other base cations (i.e., [Ca]/([Ca] + [Mg] + [Na])) in each source and well, [Ca] is the concentration of calcium, and E is the concentrating effect of evapotranspiration and exclusion. The stream water end-member was determined from a stream sample collected on each sampling date. In this system, calcium concentration was usually elevated in stream water relative to groundwater. The groundwater end-member was assumed to be the average of the well samples with the five lowest calcium concentrations; on all dates these ground water end-member wells were located at the upland-riparian boundary.

To verify that the behavior of calcium in groundwater was conservative as assumed for the mixing model, we ran the model using the stream and ground water concentrations of sodium. Using the f_{sw} and f_{gw} values obtained with calcium and the sodium concentration in stream and ground water samples, we calculated a predicted sodium concentration in the remaining wells and compared the results to the observed sodium concentration in well water.

Solute retention and production – We determined nitrate and DOC fluxes (retention or production) in the riparian zone from the difference in observed concentration in wells versus concentration predicted by the end-member mixing model. Predicted nitrate and DOC concentrations in wells were solved using equation 3. Nitrate and DOC retention/production rates (R) were translated to an area specific rate as

$$R = \frac{C_{obs} - C_{pred}}{T_{res}} Z_{gw} \qquad (4)$$

where C_{obs} is the solute concentration measured in groundwater samples, C_{pred} is the concentration predicted from the end-member mixing model (equation 3), T_{res} is residence time of the soil water in the valley bottom, and Z_{gw} is the mean depth of groundwater in the riparian zone above permafrost. Z_{gw} was assumed to be equal to the active layer depth. T_{res} was estimated by

$$T_{res} = \frac{V_{gw}}{Q_{gw}} \qquad (5)$$

where V_{gw} is the volume of soil water in the valley bottom and Q_{gw} is the discharge rate of groundwater into the stream per unit length of stream (L s^{-1} m^{-1}). V_{gw} was estimated by

$$V_{gw} = A_{vb} Z_{al} \phi \quad (6)$$

where A_{vb} is the valley bottom area, Z_{al} is the active layer depth (assuming complete saturation), and ϕ is porosity. A whole valley bottom rate of nitrate/DOC retention or production was calculated as the product of R and A_{vb}.

To calculate Q_{gw}, we conducted conservative solute slug injections at four fixed points along the stream length on four dates between June and August 2002 to measure gain in stream discharge. We injected a sodium chloride tracer upstream of a well mixed riffle and electrical conductivity was measured continuously every second at a downstream distance of 30 m from the injection point using a Campbell datalogger. The generation of a concentration-time curve allowed for the calculation of stream discharge at each point along the reach (Rantz et al. 1982). We calculated lateral inflow of groundwater from the riparian zone as the difference in stream discharge between the upstream and downstream ends of the reach. Lateral inflow expressed as L m^{-1} s^{-1} was regressed against stream discharge at the flume to develop standard curves of groundwater flow. We calculated solute retention for all dates except the late July point when the stream was flooding and discharge was much greater than was sampled by slug injection in 2002.

Denitrification assays

Denitrification rate was measured on riparian soils on five dates between May 25 and September 1, 2004 using the acetylene block technique on intact soil cores (Yoshinari and Knowles 1976) constructed of ABS pipe (3.8 cm ID x 25 cm length).

We collected soil cores from randomly-selected points to a depth of 15 cm in the valley bottom of each watershed (25 to 30 cores per watershed per date). A second core was also taken from each sampling location for analysis of soil moisture. After collecting soil, we capped soil cores with rubber stoppers. One stopper was modified with a sampling port for sampling gas in the headspace. After capping with rubber stoppers, cores were amended with 50 ml of stream water and 20 ml of acetylene (10% by total volume), and then shaken vigorously to aid equilibration between aqueous and gaseous phases. Cores were stored in a cooler to maintain the temperature near *in situ* conditions during the incubation (2 - 6 °C). Gas samples for nitrous oxide measurement were collected at 2 (initial) and 6 hours (final) following the acetylene addition with a 60 ml syringe and transferred to an evacuated serum vial until analysis. Soil cores were saved for further analysis.

We also conducted a denitrification assay in the laboratory to assess the influence of nitrate and organic carbon concentration on denitrification rate and to evaluate if field assays of denitrification were nutrient-limited due to the inhibition of nitrification by acetylene. We collected four replicate cores from 8 random locations in the valley bottom of each watershed and transported to the laboratory. Incubations were conducted at 23° C on intact cores that were amended with 50 ml of a solution containing either 1) 17 mg NO_3-N L^{-1} (as $NaNO_3$), 2) 1 g C L^{-1} (as glucose), 3) 17 mg NO_3-N L^{-1} and 1 g C L^{-1}, or 4) distilled water (control). We mixed treatment solutions in Erlenmeyer flasks and made hypoxic by attaching flasks to a vacuum line for 5 minutes. Laboratory tests showed that after 5 minutes of degassing by vacuum line, dissolved oxygen concentration

was reduced to approximately 2 mg/L. Acetylene (20 ml) was added to each sample core and then the cores were shaken vigorously to aid equilibration between gaseous and aqueous phases. As with field assays, we collected gas headspace samples at 2 and 6 hours following acetylene addition and transferred to 10 ml evacuated serum vials for later analysis.

For both the field and laboratory assays, we calculated denitrification rate as the difference between final and initial nitrous oxide concentration (corrected for gas volume in headspace, soil water volume, and nitrous oxide dissolved in aqueous phase, Bunsen coefficient = 0.02 moles N_2O L^{-1} H_2O). Nitrous oxide concentration was measured using a Varian CP-3800 gas chromatograph equipped with an electron capture detector. Following incubations, soil was dried at 95 °C in order to calculate denitrification on a soil dry mass basis. To calculate area specific denitrification rate, we divided core specific rate by the core cross-sectional area.

Laboratory analyses

We measured gravimetric soil moisture on replicate soil cores taken adjacent to denitrification assay cores (Jarrell et al. 1999). Soil organic matter content was determined from ash free dry mass (AFDM) from the difference in dry and ash-free dry mass of incubation soil. We measured soil porosity on soil cores collected on one date by adding a known volume of water to a known volume of dried soil.

Soil extractions were conducted for water extractable DOC and nitrate on replicate cores taken adjacent to the denitrification assay cores. We dried soil samples at

95° C, transferred to 200 ml plastic beakers, amended with 50 ml of nanopure water, and mixed thoroughly with a glass stirring rod. After three hours, we filtered water from the extraction using a 0.7 μm glass fiber filter.

For groundwater samples, we analyzed cations (Ca^{2+}, K^{+}, Mg^{2+}, Na^{+}, NH_4^{+}) and anions (Cl^{-}, NO_2^{-}, NO_3^{-}, PO_4^{3-}, SO_4^{2-}) on a Dionex DX-320 Ion Chromatograph. Soil extractions were only analyzed for anions. For both groundwater samples and soil extractions, we determined DOC and total dissolved nitrogen (TDN) concentration using a Shimadzu TOC-5000 analyzer plumbed to an Antek 7050 nitric oxide chemoluminescent detector. We measured conductivity on groundwater samples using a conductivity meter.

Statistics

One-way analysis of variance (ANOVA) was used to detect differences between mean stream nitrate and DOC concentrations between watersheds. Two-way ANOVA was used to detect differences in groundwater nitrate and DOC between watersheds and among sampling dates. Analysis of covariance (ANCOVA) was initially used to examine differences in thaw depth between watersheds. However, a statistically significant interaction between sampling date and watershed revealed that the slopes of the treatment regressions were not equal. Instead, a two-way ANOVA was used to detect differences in thaw depth between watersheds and among sampling dates. To validate the end-member mixing model, predicted sodium concentration was plotted against observed sodium concentration. Ninety-five percent confidence intervals were generated to

determine if the slope varied significantly from one. A two-way ANOVA was used to detect differences between observed and predicted nitrate and DOC concentrations and to detect differences between watersheds. Denitrification field assays were analyzed for significant differences between watersheds and among sample dates using a two-way ANOVA. Results from the denitrification laboratory assay were logarithmically transformed due to lack of normality and unequal variance across treatments. To detect significant differences among treatments (i.e., control, nitrate, DOC and nitrate+DOC) for the denitrification laboratory assay, a one-way ANOVA was used. Significant results from ANOVAs were further analyzed with Tukey's multiple comparison.

Results

Stream and groundwater chemistry

Stream nitrate concentration was always greater on all dates in the low permafrost watershed, averaging 34 μM compared with 22 μM in the high permafrost watershed (p = 0.008; Fig. 1a; Table 1). The concentration of nitrate in stream water was two-to three-fold greater than in riparian zone groundwater in both watersheds. Nitrate concentration in riparian zone groundwater was not significantly different between watersheds (p = 0.51) averaging 13 μM overall (Table 1). Groundwater nitrate did vary significantly among sampling dates ($p < 0.0001$).

Stream DOC concentration averaged 610 μM and 368 μM in the high and low permafrost watersheds, respectively (p = 0.20; Fig 1b). In contrast to nitrate, the concentration of DOC in riparian groundwater was two-to three-fold greater than in

stream water in both watersheds, except during a flood in July, when stream DOC concentration increased considerably in both watersheds. Comparing ground water concentration between watersheds, mean groundwater DOC concentration was significantly higher in the high permafrost watershed than the low permafrost watershed ($p = 0.002$; Fig. 1b; Table 1). DOC in riparian groundwater varied significantly among sampling dates ($p = 0.008$).

In 2003, the interaction between watershed and sampling date had a statistically significant effect on thaw depth ($p = 0.01$). In 2004, thaw depth was significantly different between watersheds ($p < 0.0001$) and among sampling dates ($p < 0.0001$). In 2003, thaw depth increased from 15 to 45 cm in the high permafrost watershed, and from 18 to 32 cm in the low permafrost watershed (Fig. 2). A similar seasonal pattern in thaw depth was observed during most of 2004.

Groundwater nitrate retention/production

The relative composition of base cations in stream and ground water samples was linearly aligned between two source waters (Fig. 3a), which, as previously described in the methods, we interpreted as two source waters contributing to riparian groundwater. The absolute concentration of calcium, however, was frequently enriched (Fig. 3b), which we interpreted in our model as enrichment due to evapotranspiration and/or exclusion. Ninety-five percent confidence intervals bounding the regression line relating predicted and observed sodium concentrations encompassed a slope of 1 (Fig. 4),

indicating that the calcium behaved conservatively and the enrichment term was warranted (Fig. 4).

In contrast to the common enrichment in calcium concentration in well water (Fig. 3b), nitrate concentration was typically below the mixing line and DOC concentration was frequently elevated or reduced (Fig. 5). The difference between predicted and observed nitrate concentration varied significantly between watersheds (p = 0.0003). For nitrate in the low permafrost watershed, the mean observed concentration of 15 μM was only 38% of the mean predicted value of 37 μM in ($p < 0.0001$; Fig. 6a). In contrast, in the high permafrost watershed, the mean observed nitrate concentration of 15 μM was not significantly different than the predicted value ($p = 0.39$). For DOC, observed concentration in groundwater was less than predicted (Fig. 6b). In the low permafrost watershed, predicted DOC concentration was significantly greater than observed ($p < 0.0001$). In the high permafrost watershed, mean DOC concentration was 1267 μM compared with a predicted concentration of 1919 μM ($p < 0.0001$).

Nitrate retention rate in the riparian zone calculated from groundwater chemistry and the end-member mixing model averaged 0.75 and 0.22 mmol N m^{-2} d^{-1} in the low and high permafrost watersheds, respectively, and was not significantly different ($p = 0.52$; Fig. 7a). DOC retention rate was not significantly different between watersheds either, averaging 31 and 19 mmol C m^{-2} d^{-1} in the low and high permafrost watersheds, respectively (Fig. 7b).

Denitrification assays

Mean denitrification rate per soil mass did not vary significantly between watersheds, averaging 136 nmol N $gSoil^{-1}$ d^{-1} in the high permafrost watershed and 90 nmol N $gSoil^{-1}$ d^{-1} in the low permafrost watershed ($p > 0.05$; Fig. 8). In the low permafrost watershed, denitrification rate varied from 31 nmol N $gSoil^{-1}$ d^{-1} in May to a maximum average of 153 nmol N $gSoil^{-1}$ d^{-1} in June. In the high permafrost watershed, denitrification rate increased from 0.21 to 378 nmol N $gSoil^{-1}$ d^{-1} from May to September. On an area basis, denitrification rate was higher in the low permafrost watershed, averaging 17 μmol N m^{-2} d^{-1} compared with 12 μmol N m^{-2} d^{-1} in the high permafrost watershed.

The denitrification laboratory assay revealed that the addition of nitrate significantly increased denitrification rate in both watersheds ($p < 0.05$; Fig. 9). Carbon amendment alone had no effect on denitrification rate in either watershed. However, the addition of carbon and nitrate together significantly increased denitrification rate in the high permafrost watershed ($p = 0.02$; Fig. 9).

Discussion

Permafrost, hydrology, and riparian zone biogeochemistry

The effect of permafrost on watershed hydrology has important consequences for stream water chemistry (MacLean et al. 1999). Permafrost prevents deep infiltration of water and confines groundwater flow to shallow organic horizons. Streams draining permafrost-dominated watersheds typically have a high dissolved organic matter (DOM)

concentration and low dissolved mineral concentrations. The absence of permafrost allows for infiltration of surface water through mineral soil, where absorption can reduce DOM in soil water (McDowell and Wood 1984). This mechanism appears to influence stream chemistry in low permafrost watersheds, where DOM concentration is typically lower than in permafrost-dominated catchments (MacLean et al. 1999). Nitrate concentration in stream water also varies with permafrost extent. In the headwater streams of CPCRW, nitrate concentration is over two-fold greater in a watershed with little permafrost (~ 3%) compared with a watershed underlain with 53% permafrost (MacLean et al. 1999, Jones et al. 2005).

MacLean et al. (1999) hypothesized that denitrification in the riparian zone is an important mechanism in regulating stream nitrogen concentration, and that in low permafrost watersheds the slow movement of subsurface water through mineral horizons allows for the greater potential for denitrification. The riparian zone functions as important control point for the flux of nutrients between terrestrial and aquatic ecosystems, in part due to denitrification (Lowrance et al. 1984, Peterjohn and Correll 1984, Cooper 1990, Naiman and Decamps 1990, Hill et al. 2000). Riparian zone soil typically has high soil moisture content, which slows the diffusion of oxygen. Typically in riparian zones, the intersection of nitrate-rich flow paths with soil rich in organic carbon promotes substantial nitrate loss via denitrification (Hedin et al. 1998, Hill 2000).

Denitrification and nitrate loss are controlled by the availability of organic carbon in headwater streams (Bernhardt and Likens 2002) and riparian zones (Hedin et al. 1998). In the boreal forest, DOC input from ground and soil water is the primary source of

carbon for stream bacterial productivity (Ford and Naiman 1989). In regions underlain with discontinuous permafrost, at least two mechanisms appear to regulate groundwater DOC concentration and input to streams. Seasonal changes in thaw depth can regulate DOC export from groundwater to streams (Carey 2003, Kawahigashi et al. 2004). As active layer depth increases from organic to mineral horizons, sorption of DOC to mineral particles can occur, reducing input to streams (McDowell and Wood 1984). The occurrence of storms can also influence DOC concentration in stream water (Bechtold et al. 2003). In the present study, stream DOC concentration spiked in both watersheds following the flood in July 2003, however, no response was detected in riparian groundwater. This observed increase in stream water was presumably due to the direct transfer of soil DOC to surface water (Hornberger et al. 1994).

Retention of groundwater nitrogen is strongly influenced by riparian vegetation (Peterjohn and Correll 1984, Groffman et al. 1992), which can retain nitrogen either directly through plant uptake or indirectly by stimulating microbial activity in the rhizosphere (Schade et al. 2001). Nitrogen retention is often elevated in riparian zones where groundwater flow is restricted to shallow subsurface flow paths that enhance the interaction with shallow organic soil and riparian plants (Peterjohn and Correll 1984, Cooper 1990, Hill 1996). In the boreal forest, the influence of plants on groundwater nitrate concentration likely occurs when the active layer confines groundwater flow to the rooting zone of plants.

Characterizing catchment hydrology is particularly difficult in regions with discontinuous permafrost, where zones of preferential flow (macropores, inter-hummock

regions, water tracks) complicate hydrologic processes (Carey and Woo 2000). Compared to the high permafrost watershed, the riparian zone of the low permafrost watershed had a shallower maximum active layer depth, higher soil moisture content, and longer residence time of water. The observation that maximum active layer depth was greater in the high permafrost watershed is somewhat surprising (Fig. 2). This difference may have been driven by differences in soil moisture in the active layer soil, which influences soil heat capacity (Hinzman et al. 1998). High soil moisture content and the greater heat capacity in the active layer of the low permafrost watershed may have reduced thawing and, thus, restricted thaw depth to relatively shallow soil horizons.

Nitrogen loss from boreal forest watersheds

Nitrogen export in streams draining boreal forest watersheds with discontinuous permafrost is greater than inputs from atmospheric deposition (Stottlemyer 1992, 1997, Jones et al. 2005). Because nitrogen limits NPP in boreal forest ecosystems (Van Cleve et al. 1983, Bonan 1990), the observed patterns of nitrogen loss are unexpected. These observations are counter to temperate forests, where watersheds tend to retain nitrogen with stream export of nitrogen being less than or equal to atmospheric deposition (Vitousek et al. 1982).

The mechanisms underlying nitrogen loss from boreal forest watersheds have not been fully characterized. However, a number of features of the boreal forest may account for this deviation from nitrogen cycling patterns observed in temperate forests (Jones et al. 2005). First, active thawing of discontinuous permafrost may release nitrogen from

previously frozen organic soil, increasing soil nitrogen pools in the boreal forest (Post et al. 1982, Osterkamp and Romanovsky 1999). Second, nitrogen-fixation rates are potentially high in boreal forest watersheds, where N-fixing alders and cyanobacteria associated with mosses are common (DeLuca et al. 2002). In either case, the capacity of the riparian zone to retain nitrogen should be important in regulating watershed nitrogen losses in streams.

To assess the importance of the riparian zone for watershed nitrogen retention in CPCRW, nitrate retention rate (estimated from the end-member mixing model) was compared to annual rates of nitrogen export in streams (using export data from Jones et al. 2005). To scale retention rates to the watershed, we multiplied riparian zone nitrogen retention rates by the fraction of the watershed accounted for by the valley bottom (less than 1% in each watershed). Relative to the nitrogen flux in stream flow, riparian nitrogen retention averaged 6 and 3 mmol N m^{-2} y^{-1} in the low and high permafrost watersheds, respectively. In the low permafrost watershed, 15% of the nitrogen moving toward the stream was retained by biological processes in the riparian zone and in the high permafrost watershed, 10% of the nitrogen was retained.

To assess the relative importance of denitrification as a mechanism for riparian zone nitrogen retention, we compared denitrification rate measured in the field to total riparian zone retention. Of the total nitrogen retained in the riparian zone, denitrification accounted for approximately 3% in both the low and high permafrost watersheds. However, we may have underestimated denitrification rate in this study. Laboratory assays revealed a strong nitrate-limitation of denitrification in the low permafrost

watershed and a significant co-limitation of denitrification by nitrate and carbon in the high permafrost watershed. The acetylene block technique tends to underestimate unamended denitrification rate because acetylene blocks nitrification as an important source of nitrate and incubations tend to disrupt natural anoxic microsites (Tiedje et al. 1989). Despite this apparent underestimation, denitrification rates measured in CPCRW are comparable to rates measured in southwest Alaska (Pinay et al. 2003), in a temperate forested ecosystem (Martin et al. 2001), and in the Sonoran Desert (Holmes et al. 1996).

Riparian zone functioning with permafrost

In conclusion, in the boreal forest, the riparian zone functions to reduce nitrate concentration in ground water. The interaction between permafrost, hydrology, and biological processes likely enhances riparian nitrate retention in this system. By confining subsurface flow to shallow organic horizons, permafrost facilitates the reduction of nitrate concentration in ground water by plant uptake and denitrification (Hill 2000). The rate of nitrogen retention in riparian zones underlain with permafrost, however, results from a complex interaction among not only the rate of nitrate and DOC supply, and the extent of anoxia, but also the rate of subsurface flow. Subsurface flow through these riparian zones appears to be complex and may be governed largely by macropores with preferential flow, which allow for rapid transport of water and solutes through the riparian zone to the stream (Carey and Woo 2000). Macropores reduce residence time of water in the valley bottom and contact time of subsurface flow with

roots and organic soil, which likely reduce the influence of plants and microbes on groundwater nitrate concentration compared with many mesic ecosystems.

Acknowledgements. We thank E. Betts, J. Eichmiller, N. Lisuzzo, and J. Rohrs for help in the field and laboratory. We thank L. Hinzman and K. Kielland, who provided valuable comments on the manuscript. This research was part of the Bonanza Creek LTER (Long-Term Ecological Research) program (funded jointly by NSF grant DEB-0423442 and USDA Forest Service, Pacific Northwest Research Station grant PNW01-JV11261952-231).

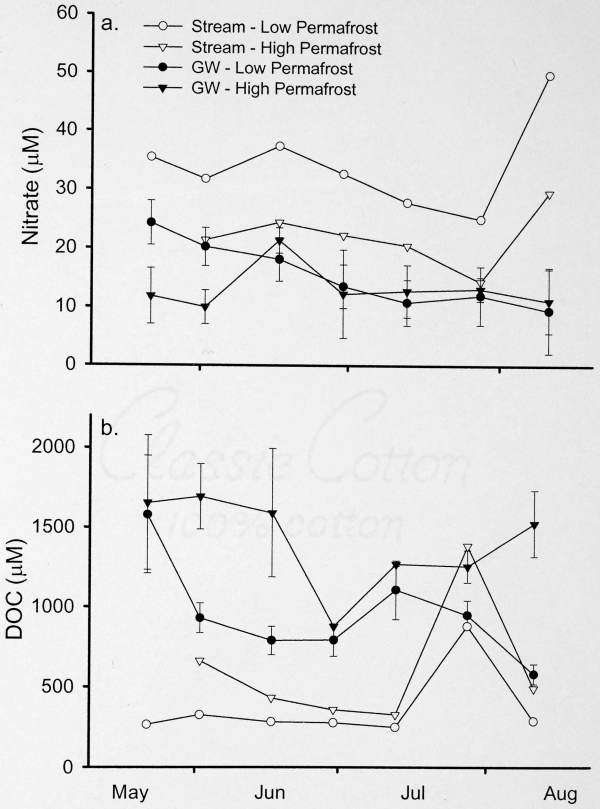

Figure 1. Temporal variation in stream and groundwater (GW) nitrate (panel a) and dissolved organic carbon (DOC; panel b) from 2003. Groundwater data points are averages (± SE) from all well samples.

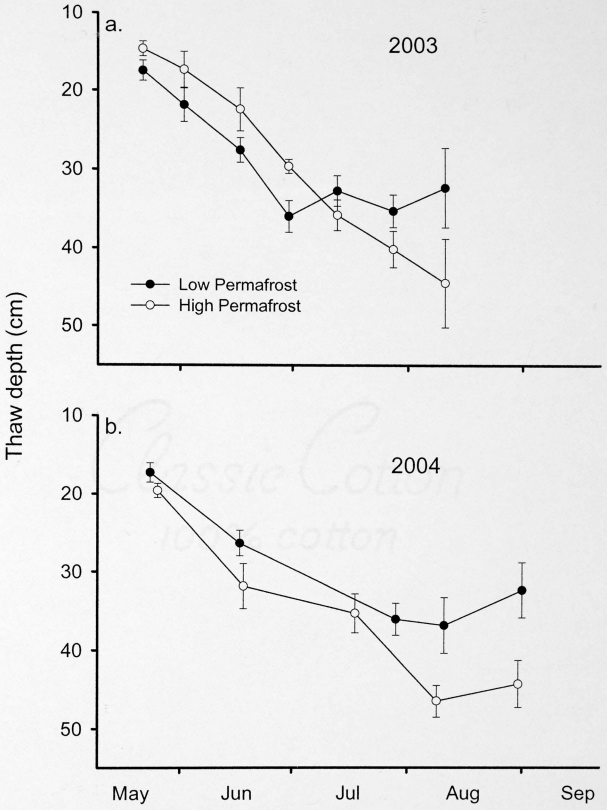

Figure 2. Seasonal variation in thaw depth in the valley bottom of the low and high permafrost watersheds in 2003 (panel a) and 2004 (panel b). Data points are averages (± SE) from all sampling points.

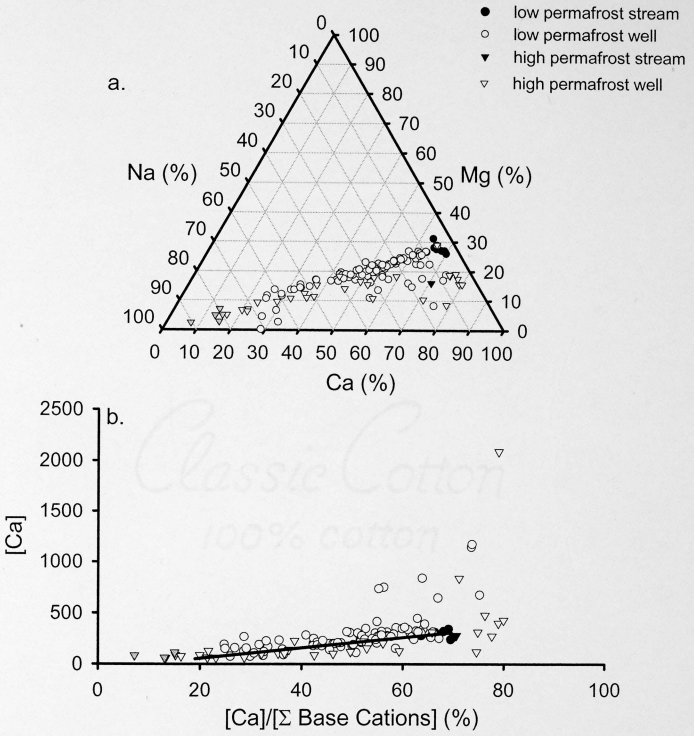

Figure 3. Ternary plot of groundwater base cation chemistry (panel a). Each axis represents the percent base cation concentration relative to the sum of all of three concentrations. Scatter plot of stream and ground water Ca concentration versus percent Ca (panel b). The black line connects mean values for groundwater end-members (shaded gray) and stream water end-members (filled symbols).

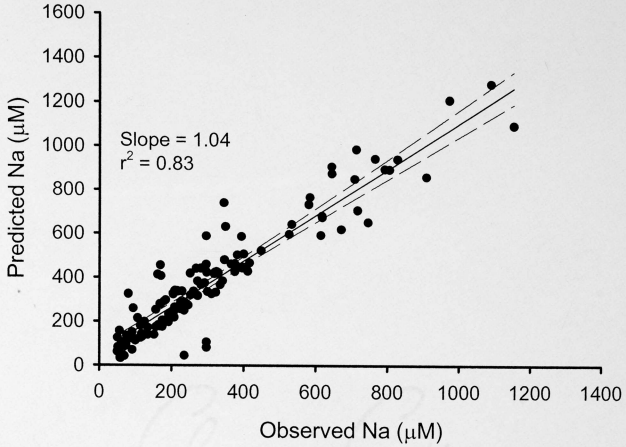

Figure 4. Relationship between observed and predicted sodium concentrations generated from the end-member mixing model. The regression line (solid) is bounded by 95% confidence intervals (dashed). The slope of the regression line is not significantly different from one, demonstrating the validity of the model.

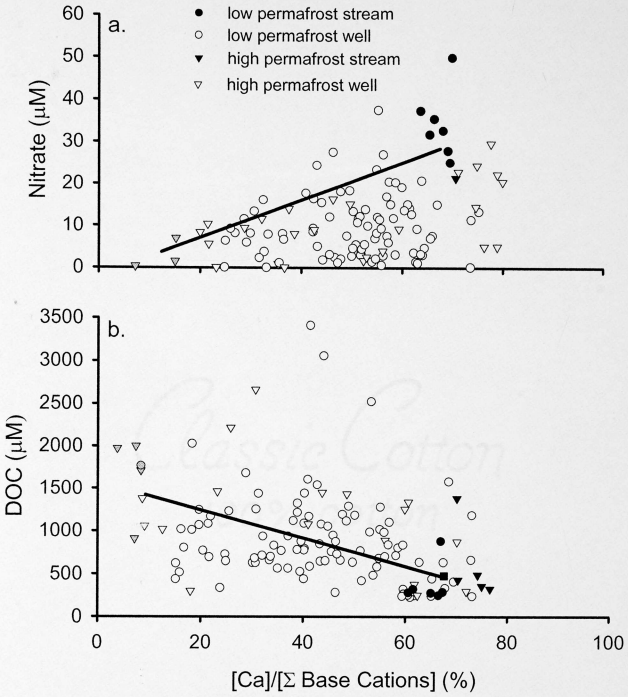

Figure 5. Scatter plot of nitrate (panel a) and DOC (panel b) versus percent Ca. Each line connects the average values for the groundwater (shaded gray) and stream water end-members and represents the predicted concentration if solutes are solely regulated by mixing of source waters.

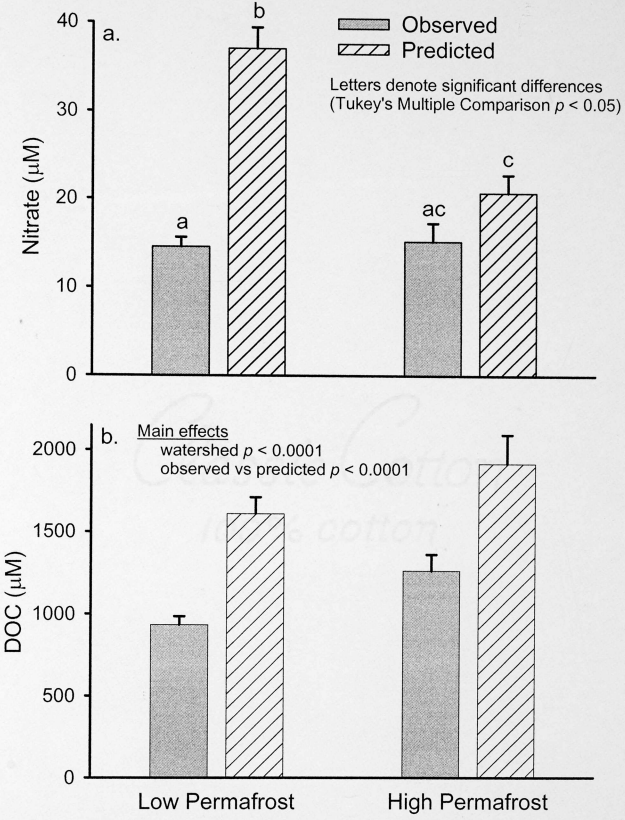

Figure 6. Predicted and observed (± SE) groundwater nitrate (panel a) and DOC (panel b) concentrations for the high and low permafrost watersheds. Predicted values were generated from an end-member mixing model.

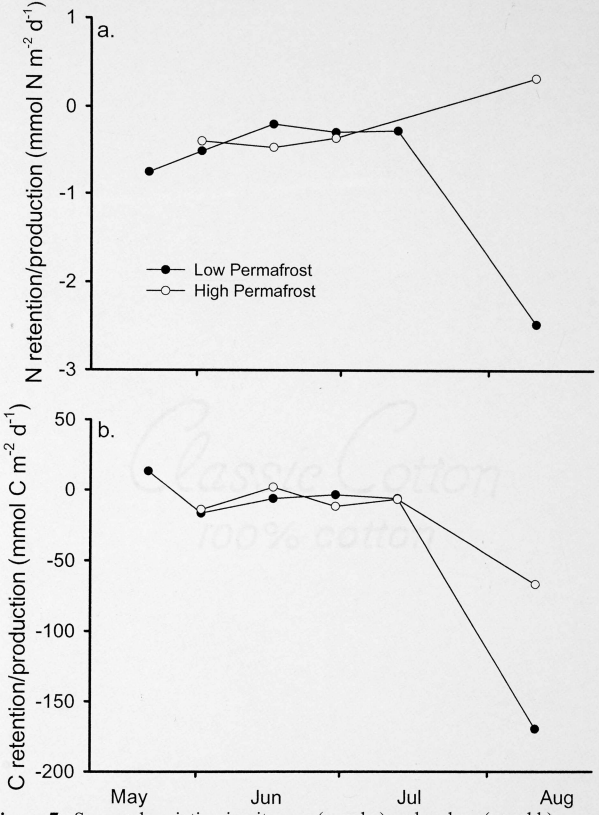

Figure 7. Seasonal variation in nitrogen (panel a) and carbon (panel b) retention/production in the riparian zone of the high and low permafrost catchments . A positive value reflects the production of groundwater nitrogen or carbon. A negative value reflects the removal of nitrogen or carbon from groundwater flow.

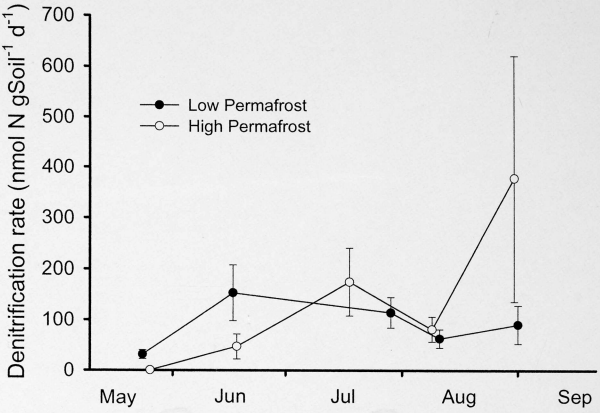

Figure 8. Seasonal variation (± SE) in denitrification rate between in the riparian zone of low and high permafrost watersheds in Caribou Poker Creek Research Watersheds.

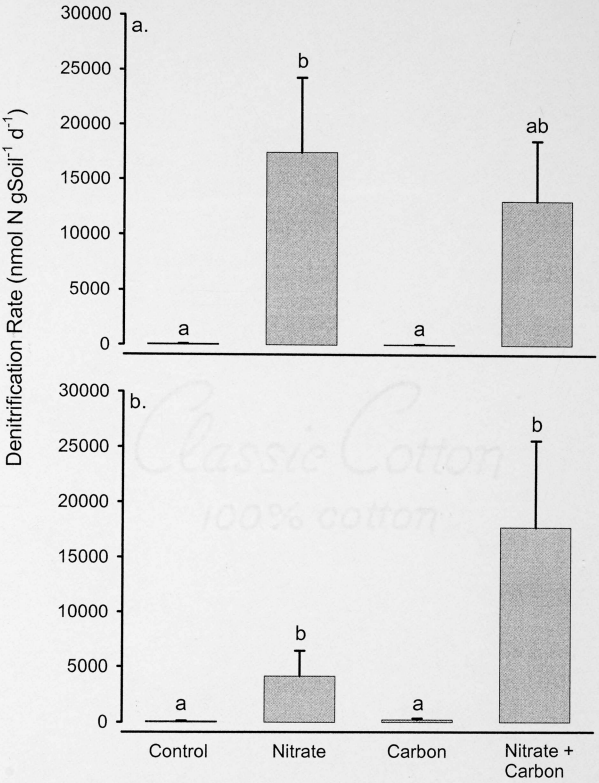

Figure 9. Denitrification rates determined from intact soil cores amended with nitrate, organic carbon, or both (n = 4 per treatment) in the low permafrost watershed (panel a) and high permafrost watershed (panel b). All treatments were made anoxic prior to acetylene addition and were replicated four times (error bars = ± SE). Bars with the same letter are not significantly different (ANOVA; $p = 0.05$).

Table 1. Summary of riparian ground and soil water solute concentrations and standard error (SE) in Caribou Poker Creek Research Watersheds in interior Alaska.

	Low Permafrost		High Permafrost	
Variable	Mean	(SE)	Mean	(SE)
Ca (μM)	309	(28)	228	(82)
Cl (μM)	158	(36)	80	(13)
DOC (μM)	1019	(57)	1494	(103)
DON (μM)	54	(3)	84	(11)
K (μM)	19	(4)	19	(6)
Mg (μM)	106	(6)	49	(9)
Na (μM)	322	(22)	498	(82)
NH_4^+ (μM)	30	(12)	8	(5)
NO_2^- (μM)	2.1	(0.2)	1.9	(0.4)
NO_3^- (μM)	12.2	(0.9)	13.7	(2.2)
PO_4^{3-} (μM)	1.3	(0.9)	0.2	(0.1)
SO_4^{2-} (μM)	128	(11)	158	(31)
Conductivity (μS cm^{-1})	91	(5)	92	(14)
Organic matter (%)	28	(2)	32	(3)
Soil moisture (%)	2.3	(0.3)	1.2	(0.1)
Water extractable DOC (μmol C g^{-1})	216	(55)	250	(64)
Water extractable nitrate(μmol N g^{-1})	3.1	(1.8)	2.1	(0.5)

References

Bechtold, J.S., R.T. Edwards, and R.J. Naiman. 2003. Biotic versus hydrologic control over seasonal nitrate leaching in a floodplain forest. Biogeochemistry 63: 53-72.

Bernhardt, E.S., and G.E. Likens. 2002. Dissolved organic carbon enrichment alters nitrogen dynamics in a forest stream. Ecology 83: 1689-1700.

Bonan, G.B. 1990. Carbon and nitrogen cycling in North American boreal forests. II. Biogeographic patterns. Canadian Journal of Forest Research 20: 1077-1088.

Carey, S.K., and M.-K. Woo. 2000. The role of soil pipes as a runoff mechanism, Subarctic Yukon, Canada. Journal of Hydrology 233: 206-222.

Carey, S.K. 2003. Dissolve organic carbon fluxes in a discontinuous permafrost subarctic alpine catchment. Permafrost and Periglacial Processes 14: 161–171.

Cooper, A. B. 1990. Nitrate depletion in a riparian zone and stream channel of a small headwater catchment. Hydrobiologia 202: 13-26.

DeLuca, T.H., O. Zackrisson, M.C. Nilsson, and A. Sellstedt. 2002. Quantifying nitrogen-fixation in feather moss carpets of boreal forests. Nature 419: 917-920.

Devito, K.J., D. Fitzgerald, A.R. Hill, and R. Aravena. 2000. Nitrate dynamics in relation to lithology and hydrologic flowpath in a river riparian zone. Journal of Environmental Quality 29: 1-14.

Ford, T.E., and R.J. Naiman. Groundwater-surface water relationships in boreal forest watersheds: dissolved organic carbon and inorganic nutrient dynamics. Canadian Journal of Fisheries and Aquatic Science 46: 41-49.

Genereaux, D.P., H.F. Hemmond, and P.J. Mulholland. 1993. Spatial and temporal variability in streamflow generation on the West Fork of Walk Branch Watershed. Journal of Hydrology 142: 137 – 166.

Groffman, P. M., A. J. Gold, and R.C. Simmons. 1992. Nitrate dynamics in riparian forests: microbial studies. Journal of Environmental Quality 21: 666-671.

Haugen, R.K., C.W. Slaughter, K.E. Howe, and S.L. Dingman. 1982. Hydrology and climatology of the Caribou-Poker Creeks Research Watershed, Alaska. CRREL Report No: 82-26, US Army Corps of Engineers, Cold Regions Research and Engineering Laboratory, Hanover, NH, USA.

Hedin, L.O., J.C. von Fischer, N.E. Ostrom, B.P. Kennedy, M.G. Brown, and G.P. Robertson. 1998. Thermodynamic constraints on nitrogen transformations and other biogeochemical processes at soil-stream interfaces. Ecology 79: 684-703.

Hill, A. R. 1996. Nitrate removal in stream riparian zones. Journal of Environmental Quality 25: 743-755.

Hill, A.R. 2000. Stream Chemistry and Riparian Zones. Pages 83-110 *in* J.B. Jones and P.J. Mulholland, editors. Streams and Ground Waters. Academic, San Diego, California, USA.

Hill, A. R., K. J. Devito, S. Campagnolo, and K. Sanmugadas. 2000. Subsurface denitrification in a forest riparian zone: interactions between hydrology and supplies of nitrate and organic carbon. Biogeochemistry 51: 193-223.

Hinzman, L.D., D.J. Goering, and D.L. Kane. 1998. A distributed thermal model for calculating soil temperature profiles and depth of thaw in permafrost regions. Journal of Geophysical Research 103: 28975-28991.

Holmes, R.M., J.B. Jones, S.G. Fisher, and N.B. Grimm. 1996. Denitrification in a nitrogen-limited stream ecosystem. Biogeochemistry 33: 125-146.

Hornberger, G.M., K.E. Bencala, and D.M. McKnight. 1994. Hydrological controls on dissolved organic carbon during snowmelt in the Snake River near Montezuma, Colorado. Biogeochemistry 25: 147-165.

Jarrell, W.M., D.E. Armstrong, D.F. Grigal, E.F. Kelly, H.C. Monger, and D.A. Wedin. Soil Water and Temperature Status. 1999. Pages 55-73 *in* G.P. Robertson, D.C. Coleman, C.S. Bledsoe, and P. Sollins. Standard Soil Methods for Long-Term Ecological Research. Oxford University Press, New York, New York, USA.

Jones, J.B., K.C. Petrone, J.C. Finlay, L.D. Hinzman, and W.R. Bolton. 2005. Nitrogen loss from watershed of interior Alaska underlain with discontinuous permafrost. Geophysical Research Letters 32:L02401, 10.1029/2004GL021734.

Kawahigashi, M., K. Kaiser, K. Kalbitz, A. Rodionov, and G. Guggenberger. 2004. Dissolved organic matter in small streams along a gradient from discontinuous to continuous permafrost. Global Change Biology 10: 1576-1586.

Lowrance, R. R., R. L. Todd, and L.E. Asmussen. 1984. Riparian forests as nutrient filters in agricultural watersheds. Bioscience 34: 374-377.

MacLean, R., M. W. Oswood, J.G. Irons, and W.H. McDowell. 1999. The effect of permafrost on stream biogeochemistry: a case study of two streams in the Alaskan (USA) taiga. Biogeochemistry 47: 239-267.

Martin, L.A., P.J. Mulholland, J.R. Webster, and H.M. Valett. 2001. Denitrification potential in sediments of headwater streams in the southern Appalachian Mountains, USA. Journal of the North American Benthological Society 20: 505-519.

McDowell, W.H., and T. Wood. 1984. Podzolization: Soil processes control dissolved organic carbon concentrations in stream water. Soil Science 137: 23-31.

Naiman, R.J., and H. Décamps, eds. 1990. The Ecology and Management of Aquatic-Terrestrial Ecotones. The Parthenon Publishing Group, Ltd, Park Ridge, New Jersey, USA.

Osterkamp, T. E., and V. E. Romanovsky 1999. Evidence for warming and thawing of discontinuous permafrost in Alaska. Permafrost and Periglacial Processes 10: 17-37.

Peterjohn, W. T., and D. L. Correll. 1984. Nutrient dynamics in an agricultural watershed: observations on the role of a riparian forest. Ecology 65: 1466-1475.

Pinay, G., T. O'Keefe, R. Edwards, and R.J. Naiman. 2003. Potential denitrification activity in the landscape of a Western Alaska drainage basin. Ecosystems 6: 336-343.

Post, W.M., W.R. Emanuel, P.J. Zinke, and A.G. Stangenberger. 1982. Soil carbon pools and world life zones. Nature 298: 156-159.

Rantz, S.E. 1982. Measurement and computation of streamflow: volume 1. measurement of stage and discharge. USGS Water Supply Paper 2175.

Rieger, S., C. E. Furbush, D.B. Schoephorster, H. Summerfield, and L.C. Geiger Jr. 1972. Soils of the Caribou-Poker Creek Research Watersheds. Cold Regions Research and Engineering Laboratory.

Schade, J.D., S.G. Fisher, N.B. Grimm, and J.A. Seddon. 2001. The influence of a riparian shrub on nitrogen cycling in a Sonoran Desert stream. Ecology 82: 3363-3376.

Schlesinger, W.H. 1997. Biogeochemistry: An Analysis of Global Change. San Diego: Academic Press.

Slaughter, C., and D. Kane. 1979. Hydrologic role of shallow organic soils in cold climates. Cold Climate Hydrology: 380-389.

Sobczak, W.V., S. Findlay, and S. Dye. 2002. Relationships between DOC bioavailability and nitrate removal in an upland stream: an experimental approach. Biogeochemistry 62: 1–19.

Stottlemyer, R. 1992. Nitrogen mineralization and streamwater chemistry, Rock Creek Watershed, Denali National Park, Alaska, USA. Arctic, Antarctic, and Alpine Research 24: 291-303.

Stottlemyer, R. 1997. Stream water chemistry in watersheds receiving different atmospheric inputs of H^+, NH_4^+, NO_3^-, SO_4^{2-}. Journal of the American Water Resource Association 33: 767-779.

Tiedje, J.M., S. Simkins, and P.M. Groffman. 1989. Perspectives on measurement of denitrification in the field including recommended protocols for acetylene based methods. Plant and Soil 114: 261-284.

Van Cleve, K., R. Barney, and R. Schlentner. 1981. Evidence of temperature control of production and nutrient cycling in two interior Alaska black spruce ecosystems. Canadian Journal of Forest Research 11: 258-273.

Van Cleve, K., L. Oliver, R. Schlentner, L.A. Viereck, and C.T. Dyrness. 1983. Productivity and nutrient cycling in taiga forest ecosystems. Canadian Journal of Forest Research 13: 747-767.

Viereck, L., C. Dyrness, K. Van Cleve, and M.J. Foote. 1983. Vegetation, soils and forest productivity in selected forest types in interior Alaska. Canadian Journal of Forest Research 13: 703-720.

Vitousek, P.M., J.R. Gosz, C.C. Grier, J.M. Melillo, and W.A. Reiners. 1982. A comparative analysis of potential nitrification and nitrate mobility in forest ecosystems. Ecological Monographs 52: 155-177.

Woo, M-K. 1986. Permafrost hydrology in North America. Atmosphere-Ocean 24: 201-234.

Yoshinari, T., and R. Knowles. 1976. Aceytlene inhibition of nitrous oxide reduction by denitrifying bacteria. Biochemical and Biophysical Research Communications 69: 705-710.

Zukowski, M.D., and M.A. Tumeo. 1991. Modeling solute transport in ground water at or near freezing. Ground Water 29: 21-25.

Conclusions

In the boreal forest, stream nitrate concentration and export vary among watersheds with varying extents of permafrost (MacLean et al. 1999, Jones et al. 2005). In this study, I examined nitrogen retention in the riparian zone as a possible source of the variation in stream nitrate concentration. Based on estimates from an end-member mixing model, riparian nitrogen retention was 10 – 15% of the loss rate observed in stream flow. Retention rates were not significantly different between the low and high permafrost watershed, suggesting that variation in stream nitrate concentration is not a function of the differences in retention rates in the riparian zone.

Denitrification accounted for a relatively small proportion of the nitrate removed from riparian groundwater. However, the acetylene block technique used in this study likely underestimated. Other lines of evidence suggest that denitrification may be an important mechanism regulating nitrate concentration in stream and ground water. Soil moisture was consistently high during the summer season, allowing for the widespread occurrence of anoxic zones conducive for denitrification. Dissolved organic carbon (DOC) concentration in riparian groundwater was high, suggesting an adequate substrate supply to fuel anaerobic metabolic processes. Also, in a laboratory assay, denitrification did not increase in response to carbon amendment. Further, spatial variation in conservative solutes such as calcium revealed that subsurface flow in the riparian zone was bidirectional. The intersection of highly oxidized, nitrate-rich stream water with reduced inland groundwater in the riparian zone likely promotes high rates of denitrification in localized hotspots (Hedin et al. 1998).

The rate of nitrogen retention in the riparian zone appears to be governed by the rate of subsurface flow. By regulating the depth of groundwater flow, permafrost indirectly controls the rate of subsurface flow through the riparian zone; flow rates through porous organic soil are considerably higher than flow through mineral soil. In addition, the occurrence macropores allows for rapid transfer of water and solutes through the riparian zone to the stream, bypassing the soil matrix (Carey and Woo 2000). Macropores decrease water residence time in the valley bottom, and, subsequently, reduce the influence of plants and microbes on groundwater nitrate concentration.

References

Carey, S.K., and M.-K. Woo. 2000. The role of soil pipes as a runoff mechanism, Subarctic Yukon, Canada. Journal of Hydrology 233: 206-222.

Hedin, L.O., J.C. von Fischer, N.E. Ostrom, B.P. Kennedy, M.G. Brown, and G.P. Robertson. 1998. Thermodynamic constraints on nitrogen transformations and other biogeochemical processes at soil-stream interfaces. Ecology 79: 684-703.

Jones, J.B., K.C. Petrone, J.C. Finlay, L.D. Hinzman, and W.R. Bolton. 2005. Nitrogen loss from watershed of interior Alaska underlain with discontinuous permafrost. Geophysical Research Letters 32:L02401, 10.1029/2004GL021734.

MacLean, R., M. W. Oswood, J.G. Irons, and W.H. McDowell. 1999. The effect of permafrost on stream biogeochemistry: a case study of two streams in the Alaskan (USA) taiga. Biogeochemistry 47: 239-267.